

**METHOD OF PREPARING COMPOUNDS USING CAVITATION
AND COMPOUNDS FORMED THEREFROM**

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Related U.S. Application Data

This application is a continuation-in-part application of U.S. Patent Application
10 Ser. No. 09/426,254 filed October 25, 1999 and claims the benefit of priority from U.S.
Provisional Patent Application Ser. No. 60/176,116 filed on January 14, 2000.

Background of the Invention

15 Cavitation is the formation of bubbles and cavities within a liquid stream resulting
from a localized pressure drop in the liquid flow. If the pressure at some point decreases
to a magnitude under which the liquid reaches the boiling point for this fluid, then vapor-
filled cavities and bubbles are formed. As the pressure of the liquid increases, vapor
condensation takes place in the cavities and bubbles, and they collapse, creating large
20 pressure impulses and elevated temperatures. Cavitation involves the entire sequence of
events beginning with bubble formation through the collapse of the bubble. Cavitation
has been studied for its ability to mix materials and aid in chemical reactions.

There are several different ways to produce cavitation in a fluid. For example, a
propeller blade moving at a critical speed through water may result in cavitation. If a
25 sufficient pressure drop occurs at the blade surface, cavitation will result. Likewise, the
movement of a fluid through a restriction such as an orifice plate can also generate
cavitation if the pressure drop across the orifice is sufficient. Both of these methods are
commonly referred to as hydrodynamic cavitation. Cavitation may also be generated in a
fluid by the use of ultrasound. A sound wave consists of compression and decompression
30 cycles. If the pressure during the decompression cycle is low enough, bubbles may be
formed. These bubbles will grow during the decompression cycle and contract or even

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implode during the compression cycle. The use of ultrasound to generate cavitation to enhance chemical reactions is known as sonochemistry.

U.S. Patent Nos. 5,810,052, 5,931,771 and 5,937,906 to Kozyuk, all of which are incorporated herein in their entirety by reference thereto, disclose improved device and methods capable of controlling the many variables associated with cavitation.

Metal-based materials have many industrial uses. Of relevance to the present invention are those solid state metal-based materials such as catalysts, piezoelectric materials, superconductors, electrolytes, ceramic-based products, and oxides for uses such as recording media. While these materials have been produced through normal co-precipitation means, U.S. Patents 5,466,646 and 5,417,956 to Moser disclose the use of high shear followed by cavitation to produce metal based materials of high purity and improved nanosize. While the results disclosed in these patents are improved over the past methods of preparation, the inability to control the cavitation effects limit the results obtained.

Summary of the Invention

One embodiment of the present invention is directed to a process for producing metal based solid state materials of nanostructured size and in high phase purities utilizing cavitation to both create high shear and to take advantage of the energy released during bubble collapse.

20 The process generally comprises the steps of: mixing a metal containing solution with a precipitating agent to form a mixed solution that precipitates a product; passing the mixed solution at elevated pressure and at a velocity into a cavitation chamber, wherein said cavitation chamber has means for creating a cavitation zone and means for controlling said zone, and wherein cavitation of the mixed solution take place, forming a
25 cavitated precipitated product; removing said cavitated precipitated product and the mixed solution from said cavitation chamber; and separating the cavitated precipitated product from the mixed solution. The present invention preferably employs an apparatus for cavitation like the apparatus described in U.S. Patent 5,937,906 to Kozyuk.

The present invention is particularly suitable for producing nanophase solid state materials such as metal oxides and metals supported on metal oxides. The synthesis of nanostructured materials in high phase purities is important for obtaining pure metal

oxides and metals supported on metal oxides for applications in catalytic processing and electronic and structural ceramics. The synthesis of such materials by cavitation results in nanostructured materials with a high phase purity. While not wishing to be bound theory, it appears that high shear causes the multi-metallics to be well mixed leading to
5 the high phase purities and nanostructured particles, and the high *in situ* temperatures results in decomposition of metal salts to the finished metal oxides or metals supported on metal oxides. The present invention may decompose at least some of the metal salts, and preferably all of the metal salts.

The present invention allows for the formation of these materials often without
10 the requirement of post synthesis thermal calcination to obtain the finished metal oxides. Conventional methods of synthesis require high temperature calcination to decompose the intermediate metal salts such as carbonates, hydroxides, chlorides etc.

The ability to synthesize advanced materials by cavitation requires the equipment used to generate the cavitation to have the capability to vary the type of cavitation that is
15 instantaneously being applied to the synthesis process stream. This “controlled cavitation” permits efficient modification of the cavitation conditions to meet the specifications of the desired material to be synthesized. The importance of the method is a capability to vary the bubble size and length of the cavitation zone, which results in a bubble collapse necessary to produce nanostructured pure phase materials. The desired
20 type of bubble collapse provides a local shock wave and energy release to the local environment by the walls of the collapsing bubbles which provides the shear and local heating required for synthesizing pure nanostructured materials. The cavitation method enables the precise adjustment of the type of cavitation for synthesizing both pure metal oxide materials as well as metals supported on metal oxides, and slurries of pure reduced
25 metals and metal alloys. A further capability of the method, which is important to the synthesis of materials for both catalysts and advanced materials for electronics and ceramics, is the ability to systematically vary the grain sizes by a simple alteration of the process conditions leading to cavitation.

Another aspect of the present invention is the formation of single metal oxides in
30 varying grain sizes of 1-20 nm, and multimetallic metal oxides in varying grain sizes and as single phase materials without the presence of any of the individual metal oxide

components of the desired pure materials situated on the surface of the desired pure material. Furthermore, the synthesis of reduced metals supported on metal oxides in both grain sizes of 1-20 nm and the capability to vary the grain sizes between 1-20 nm is also possible. Due to these unique capabilities, as compared to conventional methods of synthesis, the methods and compositions formed thereby can function as high quality catalysts, capacitors, piezoelectrics, novel titanias, electrical and oxygen conducting metal oxides, fine grains of slurries of finely divided reduced metals, and superconductors.

Brief Description of the Drawings

10 Figure 1 illustrates the variation in the strain and grain size of a piezoelectric as a function of orifice size;

Figure 2 illustrates an XRD comparison of a piezoelectric prepared according to the present invention and by classical preparation;

15 Figure 3 illustrates the XRD of finely dispersed silver on aluminum oxide synthesized in accordance with the present invention;

Figure 4 illustrates the effect of High Pressure versus Low Pressure in the cavitation process of the present invention on the synthesis of $\text{Cu}_{0.22}\text{Zn}_{0.68}\text{Al}_{0.1}\text{O}_x$;

20 Figure 5 illustrates the effect of High Pressure versus Low Pressure in the cavitation process of the present invention on the synthesis of $\text{Cu}_{0.22}\text{Zn}_{0.68}\text{Al}_{0.1}\text{O}_x$ with regard to Strain[%] versus Crystalline Size in nm;

Figure 6 illustrates the effect of High Pressure versus Low Pressure in the cavitation process of the present invention on the lattice distortion of $\text{Cu}_{0.22}\text{Zn}_{0.68}\text{Al}_{0.1}\text{O}_x$ as it relates to the c-Axis versus orifice size;

25 Figure 7 illustrates the Relative intensity of 2% Pd formed by the cavitation process of the present invention and calcined at 1095 degrees Celsius.

Description of the Preferred Embodiments

The apparatus utilized in the present invention consists of a pump to elevate the pressure of the liquid being fed to the apparatus, and a cavitation zone within the apparatus. The cavitation zone generally comprises a flow-through channel having a
5 flow area, internally containing at least one first element that produces a local constriction of the flow area, and having an outlet downstream of the local constriction; and preferably a second element that produces a second local constriction positioned at the outlet, wherein a cavitation zone is formed immediately after the first element, and an elevated pressure zone is created between the cavitation zone and the second local
10 constriction.

The liquid is preferably pressurized prior to entering the flow-through channel. A local constriction in the channel creates an increase in the velocity of the liquid flow to some minimum velocity, creating a sufficient pressure drop to allow cavitation to occur.
15 On average, and for most hydrodynamic liquids, the minimum velocity is 16 m/sec or greater.

The element(s) producing the local constriction may take many different shapes. It may be of the form of a cone, or spherical or elliptical shape, and can be located in the center of the flow channel. It is possible to use a crosshead, post, propeller, nozzle or any other fixture that produces a minor loss in pressure. Preferred is one or more orifices or
20 baffles. By varying the size of the orifice, the apparatus is able to better control the size of the cavitation bubbles being formed. The orifice may have one or more circular or slotted openings.

The cavitation bubbles then are transported by the flow of liquid immediately into a cavitation zone, which comprises numerous cavitation bubbles. The cavitation bubbles
25 flow with the liquid into an elevated pressure zone. By having a second element in the flow channel downstream of the cavitation zone, a back pressure is created to form the elevated pressure zone. The second element can also take many shapes, but an element similar in operation to a control valve is preferred. By controlling the pressure in this zone, the apparatus is able to determine the length of the cavitation zone and determine
30 when bubble collapse will occur. Upon entering the elevated pressure zone, the cavitation bubbles collapse, resulting in high pressure implosions with the formation of

shock waves that emanate from the point of each collapsed bubble. Under the high temperatures and pressures caused by bubble collapse, the liquid on the boundary of the bubble, and the gas within the bubble itself, undergo chemical reactions depending upon the materials in the feed. These reactions may be oxidation, disintegration or synthesis,

5 to name a few.

In another aspect of the invention, the second element can be the first element of a second cavitation zone. In this manner two or more cavitation zones may be placed in series to produce a multi-stage apparatus. Each cavitation zone is controllable depending on the first element selected for the next cavitation zone, the distance between each first 10 and second element, and by the final second element at the end of the multi-stage apparatus.

In yet another aspect of the invention, the second element can be as simple as a 15 extended length of the channel, a turn or elbow in the channel, or another piece of processing equipment. The second element must provide some back pressure to create the cavitation and elevated pressure zones.

The desired cavitated products are then removed from the liquid by suitable separation techniques, such as vacuum filtration, filtration and evaporation. Prior to or after removal of the cavitated products, the liquid may be recycled back to the cavitation chamber. Recycle of the unfiltered product may occur many times. Where multi-stage 20 cavitation chambers are used, recycle may be to one or more of the chambers. As the length of the period of recirculation increases, the resulting final product generally has a higher degree of phase purity and smaller particle size.

The nanostructured materials of the present invention are typically prepared by precipitation of the desired product from a metal containing solution. The metal 25 containing solution normally is aqueous, but can be non-aqueous. At least one component of the metal containing solution must be in a liquid state and be capable of creating cavitation. Other components may be different liquids, solids, gasses, or mixtures thereof. The liquid component could be materials commonly thought of as liquid, or can be materials commonly thought of as solid or gas being processed in their liquid state. Examples of such materials are molten metals and molten minerals, as long as the vapor 30 pressure is sufficiently low enough to generate bubbles, and liquid carbon dioxide.

Most metals are in the form of salts. However, in the case of certain precious metals the metal may be added in the form of an acid such as chlorplatinic acid. Examples of suitable salts include nitrates, sulfates, acetates, chlorides, bromides, hydroxide, oxylates and acetylacetones. The metal may be cobalt, molybdenum, 5 bismuth, lanthanum, iron, strontium, titanium, silver, gold, lead, platinum, palladium, yttrium, zirconium, calcium, barium, potassium chromium, magnesium, copper, zinc, and mixtures thereof, although any other metal may find use in the present invention. For example, iron oxide may be made from ferric nitrate hydrate, barium titanate from a mixture of barium acetate in water and titanium tetraisopropoxide in isopropyl alcohol, 10 and a ceramic such as lanthana from lanthanum nitrate. Complex metal catalysts such as iron bismuth molybdate may be formed utilizing the appropriate metal salts.

A class of metals typically suited for piezoelectric, materials are lanthanum, titanium, gold, lead, platinum, palladium yttrium, zirconium, zinc and mixtures thereof.

A class of metal typically suited for superconductors are strontium lead, yttrium, copper, 15 calcium, barium and mixtures thereof. The solution into which the salt is dissolved will depend upon the particular metal salt. Suitable liquids include water, aqueous nitric acid, alcohols, acetone, hydrocarbons and the like. The precipitating agent may be selected from any suitable basic material such as sodium carbonate, ammonium carbonate, potassium carbonate, ammonium hydroxide, alkali metal hydroxide or even water where 20 the metal salt reacts with water. Any liquid which causes the desired metal salt to precipitate from solution due to insolubility of the metal salt in the liquid may be a precipitating agent.

In the embodiments where recycling occurs, it is desirable that the pH of the mixed solution be maintained on the basic side, usually between 7.5-12. However, the 25 range is dependent on the precise material being synthesized.

In the case of preparing catalysts, a support may be added directly to the metal containing solution, the precipitating agent or both. Suitable supports include alumina, silica, titania, zirconia and alumino-silicates. The support may also be added in the form of a salt, such as alumina being added as aluminum nitrate hydrate where the support 30 itself is precipitated in the form of nanostructured grains under cavitational conditions.

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Zeolites such as ZSM-5, X-Type, Y-Type, and L-Type may be prepared using the process of the present invention. Metal loaded zeolitic catalysts typically contain a metal component such as platinum, palladium, zinc, gallium, copper or iron. The metal salt solution, the precipitating agent and a silica source may be premixed to form a zeolite gel prior to passing to the cavitation chamber. Where the gel requires heat to form, the mixture may be recycled in the cavitation chamber until the gel forms and the synthesis results. Alternately, after cavitation, the well dispersed gel may be placed in a conventional autoclave where a hydrothermal synthesis is carried out. This method will result in much finer grain zeolites after the conventional hydrothermal treatment.

10 The process of the present invention has applicability to catalysts, electrolytes, piezo-electrics, super-conductors and zeolites as examples of nanostructured materials.

The following examples show the benefit of the present process in the production of nanosize high purity products. Two apparatuses were used in these examples. The Model CaviPro™ 300 is a two stage orifice system operating up to 26,000 psi with a nominal flow rate of 300 ml/min and up. The CaviMax™ CFC-2h is a single orifice system operating up to 1000 psi with a nominal flow rate of several liters per minute. Both of these devices are obtainable from Five Star Technologies Ltd, Cleveland, Ohio. Modifications were made to the peripheral elements of these devices, such as heat exchangers, cooling jacket, gauges and wetted materials, depending on the application contained in the examples.

Example 1

This example illustrates that controlled cavitation enables the synthesis of an important hydrodesulfurization catalyst for use in the environmental clean-up of gasoline in a substantially improved phase purity as compared to conventional preparations. The preparation of cobalt molybdate with a Mo/Co ratio of 2.42 was carried out in the CaviPro™ processor. Different orifice sizes were used for the experiment at a hydrodynamic pressure of 8,500 psi. In each experiment 600ml of 0.08M of ammonium hydroxide in isopropanol was placed in the reservoir and recirculated. While this precipitating agent was recirculated, a mixture of 3.43g (0.012 mol) of $\text{CoNO}_3 \cdot 6\text{H}_2\text{O}$ and

5.05g (0.029 mol) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in 50ml of distilled water was metered in over 20 minutes. After the salt solution had been added, the resulting slurry was immediately filtered under pressure and dried for 10 hours at 110°C. XRD analyses were recorded after air calcination at 325°C.

5 The conventional preparation of cobalt molybdate with a Mo/Co ratio of 2.42 was
carried out in classical synthesis. In each experiment 600ml of 0.08 M of ammonium
hydroxide in isopropanol was placed in a well stirred vessel. While this precipitating
agent was stirred, a mixture of 3.43g (0.012mol) of $\text{CoNO}_3 \cdot 6\text{H}_2\text{O}$ and 5.05g (0.029mol)
 $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in 50 ml of distilled water was metered in over 20
10 minutes. After the salt solution had been added, the resulting slurry was immediately
filtered under pressure and dried for 10 hours at 110°C. XRD analyses were recorded
after air calcination at 325°C. The XRD pattern of the material after calcining in air
indicates, by the high intensity of the reflection at 26.6 degrees 20 in all of the syntheses
using cavitation processing, the formation of a high fraction of cobalt molybdate.
15 Furthermore, the XRD of the conventional method demonstrated a much lower intensity
peak at 26.6 degrees 20 as well as strong reflections at 23.40 and 25.75 degrees 20 due to
separate phase MoO_3 . Thus the present process produced a higher purity catalyst than
found in the prior art.

Example2

The catalyst of Example I was repeated but at a higher hydrodynamic pressure of 20,000 psi. XRD patterns showed even higher phase purity as compared to the cavitation preparation in Example 1 and much better purity as compared to the classical synthesis.

Example 3

The catalyst of Example 1 was prepared using a CaviMax processor at a lower pressure. The orifice used was 0.073 inches diameter at 580 psi head pressure. The back pressure was varied between 0-250 psig. The phase purity of cobalt molybdate was nearly as high as that observed in Example 2 and much better than that observed in

Example 1. It was much better than the conventional preparation that did not use hydrodynamic cavitation. The XRD data shows that the application of all back pressures resulted in higher purity phase of cobalt molybdate as compared to the conventional preparation.

5

Example 4

Example 1 was repeated using a CaviMax™ processor at a pressure of 200-660 psi. and using orifice sizes of 0.073, 0.075, 0.089, and 0.095 inches diameter. The phase purities of the catalysts were all improved. The use of an orifice diameter of 0.095 inches at 280 psi resulted in a superior quality hydrodesulfurization catalyst as compared to all of the other diameters as well as the conventional synthesis.

15 Example 5

This example illustrates the capability of the present invention to synthesize high phase purities of cobalt molybdate supported on gamma-alumina. The preparation of cobalt molybdate deposited on gamma-alumina with a Mo/Co ratio of 2.42 was carried out in the CaviPro™ processor. A cavitation generator having 0.009/0.010 inch diameter orifice sizes was used for the experiment at a hydrodynamic pressure range of 4,000, 7,000, and 8,000 psig. In each experiment 600ml of a solution of 0.0102% ammonium hydroxide in isopropyl alcohol (IPA) was placed in the reservoir along with 5.0g of gamma-alumina, and the slurry was recirculated through the processor. While this precipitating agent was recirculated, 0.859g (0.00295 mol) of $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 1.262g (0.000715 mole) of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in 50ml of water was metered in over 20 minutes. After all of the salt solutions had been added, the resulting slurry was recirculated through the processor for an additional 5 minutes. The slurry was immediately filtered under pressure and dried for 10 hours at 110°C. XRD analyses were recorded after air calcination at 350°C for four hours.

30 At all pressures the experiment resulted in superior phase purities of the active hydrodesulfurization catalyst precursor, cobalt molybdate, as compared to the

conventional synthesis of the same catalyst. In addition, for this catalyst, the optimum conditions for the generation of the smallest nanostructured grains of the catalyst resulted from the low pressure, 4,000 psi synthesis.

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Example 6

The catalyst of Example 5 was prepared using silica in place of alumina. The preparation of cobalt molybdate deposited on Cabosil (silica) with a Mo/Co ratio of 2.42 was carried out in the CaviPro processor. Different orifice sizes were used for the 10 experiment at a hydrodynamic pressure range of 10,000 psi. In each experiment 600ml of 0.0102% ammonium hydroxide in isopropyl alcohol (IPA) was placed in the reservoir along with 5.0g of Cabosil, and the slurry was recirculated through the processor. While this precipitating agent was recirculated, 0.859g (0.00295 mol) of $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 1.262g (0.000715 mol) of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in 50ml of water was metered 15 in over 20 minutes. After all of the salt solutions had been added, the resulting slurry was recirculated through the processor for an additional 5 minutes. The slurry was immediately filtered under pressure and dried for 10 hours at 110°C. XRD analyses were recorded after air calcination at 350°C for four hours.

The cavitation synthesis resulted in higher phase purity for cobalt molybdate 20 deposited on silica as compared to the conventionally prepared catalyst, and the use of a 0.006 and 0.014 inch diameter orifice set led to finer nanostructured grains of the catalyst.

Example 7

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The present invention was used to synthesize beta-bismuth molybdate ($\text{Bi}_2\text{Mo}_2\text{O}_9$), which is typical of the family of catalysts used for hydrocarbon partial oxidations such as the conversion of propylene to acrolein or ammoxidation of propylene to acrylonitrile. This synthesis used a CaviMax™ processor with four different orifice 30 sizes in a low pressure mode. The synthesis of this material was carried out as follows. 450ml of IPA was used as the precipitating agent, and was placed in the reservoir. While

this precipitating agent was recirculated, 12.83g, 0.0264 mol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ dissolved in 50ml of 10% HNO_3 , and 4.671g, 0.00378 mol of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ dissolved in 50ml of distilled water was metered in over 20 minutes. After all of the salt solutions had been added, the resulting slurry was recirculated through the processor for an additional 2 minutes. The slurry was immediately filtered under pressure and dried for 10 hours at 110°C. XRD analyses were recorded after air calcination at 350°C.

Table 1: Variation of Grain Sizes

Orifice Diameter (in.)	Crystallite Grain Size (nm)
0.073	21
0.081	28
0.089	22
0.095	11

The cavitational syntheses resulted in very pure phase beta-bismuth molybdate. Furthermore, the XRD patterns showed that the grain size of the particles could be varied over a wide range of nanometer sizes by changing the orifice sizes. Since it is well known in the catalytic literature that nanometer grains of catalysts often result in greatly accelerated reaction rates, the capability of the cavitational syntheses to vary this grain size is of general importance to several catalytic reactions other than hydrocarbon partial oxidation.

Example 8

This example shows that the present invention as applied to the synthesis of complex metal oxides such as perovskites and ABO_3 metal oxides results in unusually high phase purities. The synthesis of $\text{La}_{0.7}\text{Sr}_{1.3}\text{FeO}_3$ was performed using a CaviMax™

processor and using orifice sizes of 0.073, 0.081, 0.089, and 0.095 inch diameter. 600ml of a 1M solution of Na_2CO_3 in distilled water was placed in the reservoir, and the slurry was recirculated through the processor. While this precipitating agent was recirculated, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (7.999g, 0.0185 mol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (10.662g, 0.0264 mol) and
5 $\text{Sr}(\text{NO}_3)_2$ (1.6755g, 0.00792 mol) were dissolved in 100ml of distilled water and this solution was metered in over 20 minutes. After all of the salt solutions had been added, the resulting slurry was recirculated through the processor for an additional 5 minutes. The slurry was immediately filtered under pressure and dried for 10 hours at 110°C. XRD analyses were recorded after air calcination at 600°C.

10 The XRD data showed that an orifice size of 0.095 inches diameter resulted in the synthesis of nanostructured pure phase perovskite, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{1.0}\text{O}_{3.0-x}$, as a nanostructured material of 18 nm and the phase purity was much better than that attainable by the conventional synthesis. Parallel experiments using the CaviPro™ processor using orifice sets of 0.006/0.008, 0.006/0.010, 0.006/0.012 and 0.006/0.014
15 inch diameter all resulted in very pure phases of the desired perovskite containing little separate phase impurities. These results were superior to both the CaviMax™ and conventional synthesis. The importance of this type of perovskite material is for CO oxidation in automotive exhaust emissions applications, for solid state oxygen conductors for fuel cells applications, and for dense catalytic inorganic membranes used for oxygen
20 transportation in the reforming of methane to syngas.

Example 9

This example shows that strain can be systematically introduced into a solid state crystallite by use of the present invention. The example examined the synthesis of 5 titanium dioxide using the CaviMax™ processor and examined the effect of strain introduced into the TiO₂ crystal as the orifice size of the cavitation processor was systematically changed. In this synthesis 100g (0.27664 mol) Ti-Butoxide was mixed with 2-Propanol to give a volume of 0.5 l (Molarity = 0.553 mol/l) in a glove-box under nitrogen. This process yielded a clear yellowish solution, which is stable in air. 750ml of 10 deionized water was placed for a typical run in the reservoir of the CaviMax and circulated. 75ml of the Ti-Butoxide/2_Propanol solution was added slowly with a feed rate of 4 ml/minute. The solution with the precipitated Ti-compound was circulated for an additional 17 minutes. Afterwards the slurry was high pressure filtered at 100 psi (6.9 bar). The filtrate was dried at 100°C for 2 hours and then calcined at 400°C for 4 hours. 15 The XRD data were taken after air calcination and the percent strain was estimated from the Williamson-Hall method.

Table 2: Crystallite Strain

Orifice Size (inches)	Strain %
0.073	0.26
0.081	0.23
0.089	0.26
0.095	0.29
0.105	0.32
0.115	0.33
0.230	0.43

As shown in Table 2, the strain content of the crystallites increased from 0.2% prepared with a small orifice (0.073 inches diameter) to 0.35% prepared with a large orifice (0.115 inches diameter), linear with its diameter. The ability to systematically alter the strain within a crystallite is important due since it changes the chemical potential of the surface atoms. Applications of this type of control include the application of these materials as photocatalysts and as optical absorbers.

Example 10

10

The synthesis of 20% w/w Ag on titania of nanostructured metallic silver was examined as a function of orifice size, and the results were compared to the conventional synthesis of such metal supported materials. In this synthesis, a precipitating agent consisting of 1000 ml of deionized water was recirculated in the CaviMax™ processor equipped with a 0.075 inch diameter orifice. A 100ml solution of titanium (IV) butoxide ($Ti[O(CH_2)_3CH_3]_4$) in isopropyl alcohol (0.63 mol/L Ti) was added to the CaviMax™ at 4 ml/min to form a precipitate. The total time of precipitation plus additional recirculation was 30 minutes. Afterwards, two solutions were added simultaneously to the recirculating, precipitated titanium slurry. The first solution consisted of a 250ml silver solution of silver acetate ($AgOOCCH_3$) in deionized water (0.046 mol/L Ag), which was added at a rate of 10 ml/min. The second feed was a 250ml solution of hydrazine (N_2H_4) in water (0.70 mol/L N_2H_4), such that the N_2H_4/Ag molar ratio was 15.0, which was added at a rate of 10 ml/minute. The total time of addition plus additional recirculation was 30 minutes. The product was filtered, washed with water to form a wet cake, and then dried in an oven at 110°C. A portion of the dried product was calcined in air for 4 hours at 400°C. A portion of the dried product was submitted for x-ray analysis and identified as silver on an amorphous titanium support. X-ray line broadening analysis indicated that the mean silver crystallite size was 7.4 nm. A portion of the calcined product was submitted for x-ray analysis and identified as silver on titania. All of the titania was identified as anatase, while no rutile was observed. X-ray

line broadening analysis indicated that the mean silver crystallite size was 12.0 nm. The conventional synthesis was performed as above except in a stirred 1500 ml beaker.

The grain sizes of the silver particles after drying the samples at 110°C are shown in Table 3. This example shows that metallic particles deposited on reactive supports such as titania can be synthesized in smaller grain sizes as compared to parallel conventional synthesis. Furthermore, when the catalysts were calcined to 400°C in air, the silver particles deposited on the conventional catalyst grew to a much larger size than those deposited by cavitational techniques. These types of materials are important as photocatalysts for the destruction of toxins in waste chemical streams.

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Table 3: Grain Size of 20% w/w Silver on Titania

	Grain size, dried (nm)	Grain Size, Calcined 400°C
Conventional Precipitation-Deposition	7.6	20.1
CaviMax 0.115 orifice	4.7	13.4
CaviMax 0.073 orifice	7.4	12.0

Example 11

15 2% w/w silver was synthesized on alpha-alumina using both a cavitational synthesis and a conventional synthesis. The synthesis of this material was carried out as follows.

A slurry consisting of 5.00g of aluminum oxide (alpha, Al₂O₃) in 1000 ml deionized water was recirculated in the CaviMax processor equipped with a 0.073 inch 20 diameter orifice. Two solutions were added to the recirculating aluminum oxide slurry. The first solution consisted of a ml solution of silver acetate (AgOOCCH₃) and ammonium hydroxide (NH₄OH) in deionized water. The concentration of the silver was 0.0095 mol/L, and the concentration of ammonium hydroxide was 0.095 mol/L, so that

the NH₄OH/Ag molar ratio was 10.0. The silver solution was added to the aluminum oxide slurry at a rate of 4 ml/minute. The second feed was a 100ml solution of hydrazine (N₂H₄) in water (0.14 mol/L N₂H₄), such that the N₂H₄/Ag molar ratio was 15.0, which was added at a rate of 4 ml/minute. The total time of addition plus additional recirculation was 30 minutes. The product was filtered, washed with water to form a wet cake, and then dried in an oven at 110°C. A portion of the dried product was submitted for X-ray analysis and identified as silver on alpha alumina. Conventional synthesis was performed in the same manner as above except in a stirred 1500ml beaker.

5 The data in Table 4 show that the cavitation synthesis using an orifice size of 0.073 in. diameter and a 10/1 NH₄OH/Ag ratio resulted in much smaller grain sizes of 10 Ag.

Table 4: Grain sizes (nm) of 2% Ag/Al₂O₃ synthesis

2%Ag/titania	10:1 NH ₄ OH:Ag
Conventional Synthesis	20.9 nm grains
CaviMax 0.073 in. dia.	14.0 nm grains

15 Example 12

The present invention was utilized for the synthesis of nanostructured particles of gold supported on titanium oxide (TiO₂). In this synthesis a precipitating agent consisting of 650ml of deionized water was recirculated in the CaviMax™ processor equipped with a 0.075 inch diameter orifice. A 100ml solution of titanium (IV) butoxide (Ti[O(CH₂)₃CH₃]₄) in isopropyl alcohol (0.88 mol/L Ti) was added to the CaviMax™ at 4 ml/minute to form a precipitate. The total time of precipitation plus additional recirculation was 37.75 minutes. Immediately after, two solutions were added simultaneously to the recirculating, precipitated titanium slurry. The first solution consisted of a 1000ml gold solution of chloroauric acid (HAuCl₄ 3H₂O) in deionized water (0.0073 mol/L Au), which was added at a rate of 4.7 ml/minute. The second feed was a 100ml solution of hydrazine (N₂H₄) in water (0.12 mol/L N₂H₄), such that the N₂H₄/Au molar ratio was 16.7, which was added at a rate of 0.4 ml/minute. The total time of addition plus additional recirculation was 3.62 hours. The product was filtered,

washed with water to form a wet cake, and then dried in an oven at 110°C. A portion of the dried product was calcined in air for 4 hours at 400°C. A portion of the calcined product was submitted for x-ray analysis and identified as gold on titania (anatase). X-ray line broadening analysis indicated that the mean gold crystallite size was 7.5 nm, and
5 that the mean anatase crystallite size was 12.9 nm. Conventional synthesis was prepared in the manner above except in a stirred 1500ml beaker.

The data in Table 5 shows that cavitation processing during the synthesis of 2% w/w of gold on titania results in systematically decreasing, grain sizes into the very small manometer size range. This example shows that the combination of orifice size selection
10 and process parameters afford a control of grain sizes not possible with conventional synthesis.

Table 5: Grain size as a function gold solution volume

Gold conc. (mol/L)	Volume of Au soln. (mL)	H ₂ NNH ₂ feed rate (mL/min)	Titania grain size (nm)	Gold grain size (nm)
0.0145	50	8.0	12.5	78.6
0.0073	100	4.0	11.6	33.6
0.0036	200	2.0	11.4	27.9
0.0018	400	1.0	12.0	16.0
0.0007	1000	0.4	12.9	7.5

Where cavitation synthesis gave a 16 nm Au grain size, conventional synthesis
15 resulted in a grain size of 25 nm. Where cavitation synthesis gave a 7.5 nm Au grain size, conventional synthesis gave a grain size of 23 nm.

Example 13

20 The present invention was used to synthesize commercially important piezoelectric solid state materials in very high phase purities at low thermal treating temperatures.

Table 6: Preparation of PZT in different stoichiometries

Ratio Zr : Ti	ZrBut [ml]	TiBut [ml]	Sum Formula
30 : 70	15	35	Pb(Zr _{0.3} Ti _{0.7})O ₃
40 : 60	20	30	Pb(Zr _{0.4} Ti _{0.6})O ₃
50 : 50	25	25	Pb(Zr _{0.5} Ti _{0.5})O ₃
60 : 40	30	20	Pb(Zr _{0.6} Ti _{0.4})O ₃

Four solutions were prepared to synthesize PZT. 105.95g (0.279 mol) Pb(II)acetate trihydrate (PbAc) were dissolved in 1000ml purified water. 100g (0.279 mol) Ti-Butoxide (TiBut, 97%) were diluted with 2-Propanol to 500ml. 132.58g (0.279 mol) Zr-Butoxide-Butanol-Complex (ZrBut, 80%) was diluted with 2-Propanol to 500ml. 2.74g (0.0285 mol) of ammonium carbonate (Amm) was solved for each run in 350ml water to give a 0.0814M solution. The detailed stoichioinetric information for this series is given in Table 6. The ammonium carbonate solution was placed in the reservoir and circulated. The Zr and Ti solutions were combined and fed at a rate of 2.5 ml/minute into the reservoir stream at a position just before the inlet to the high pressure, pump. The Pb-acetate solution was co-fed with a rate of 5 ml/minute. All of the metal containing components immediately precipitated and were drawn into the high pressure zone of the cavitation processor and then passed into the cavitation generation zone. All samples were dried over night and calcined in three steps for four hours at 400°C, 500°C and 600°C. XRD patterns illustrated that above a calcination temperature of 500°C only the pure perovskite phase is formed with no lead oxide or zirconium oxide impurities. The XRD patterns contains some finer crystallites of this material appearing as a broad band centered at 30 degrees 2θ. This material disappears from the composition after calcination to 600°C.

Furthermore, this material of the present invention showed a much higher phase purity. The data in Figure 1 illustrates that the hydrodynamic cavitation technique enables the synthesis of piezoelectrics in compositions having a very high degree of strain built into the individual crystallites. Furthermore, Figure 1 shows that the degree of strain can be systematically introduced into the crystals as a function of the type of orifice used in

the synthesis. It was found that the degree of strain introduced by cavitation was much greater than that found in a classical method of piezoelectric synthesis of the same composition.

The data in Figure 2 illustrates the advantage of cavitated processing in PZT synthesis by a direct comparison to a classical co-precipitation synthesis. The top XRD pattern in Figure 2 resulted from a cavitated preparation after 600°C air calcination. The lower figure resulted from a classical co-precipitation carried out using the same synthesis procedure except that only high speed mechanical stirring was used in the co-precipitation step rather than cavitated processing. A comparison of the two XRD patterns shows that the classical pattern has a substantial fraction of separate phase lead oxide while the cavitated preparation has no secondary phase in its composition. This higher phase purity is exceptionally important to the functioning of the materials as a piezoelectric device.

Example 14

15 The present invention was utilized for the synthesis of fine particles of pure metallic particles in a slurry where the grain size can be altered depending upon the orifice sizes being used. The data in Table 7 illustrates the capability to form nanostructured grains of finely divided metals typically used commercially to

20 hydrogenate aromatics and functional groups on organic intermediates in fine chemical and pharmaceutical chemical processes. In this synthesis Hexachloroplatinic acid was dissolved 0.465g in 50ml isopropanol. This platinum solution was fed to a stirred Erlenmeyer flask, containing 0.536g hydrazine hydrate, 54.7% solution in 50ml isopropanol. The platinum solution feed rate was 5ml/minute. Directly following the 25 platinum reduction, the solution was fed to the CaviPro processor, and processed for 20 minutes, after which time the XRD of the dried powders were measured.

Table 7: Effect of pressure and orifice sizes on the synthesis of nanostructured platinum

Orifice set	Pressure	Pt metal grain size (nm)
.004/.014	25,000 psi	3.9
.004/.006	25,000 psi	3.7
.004/.014	15,000 psi	4.1
.004/.006	15,000 psi	3.9
Classical	14.7 psi	5.4

Example 15

5

The process of the present invention was used to fabricate the commercially important silver on α -alumina catalysts used in the production of ethylene oxide from the partial oxidation of ethylene. The data in Table 8 illustrates the XRD determined grain sizes of the silver particles which had been deposited onto α -alumina during the

10 cavitation synthesis in which the silver was reduced in a cavitation experiment and then deposited onto the α -alumina in water using classical techniques. The data shows that changing the orifice sizes used in each experiment can alter the grain size of the silver.

15 The characteristics of the different orifice sizes are expressed as the throat cavitation numbers calculated for each experiment, which is a common reference for the occurrence of cavitation in flowing fluid streams. Using this method of characterization, the cavitation generated in the metal synthesis stream is higher as the throat cavitation numbers decreases.

In this synthesis, 2% silver on α -alumina was prepared by the reduction of silver acetate using hydrazine. This reduction was conducted in the CaviPro™ processor at a 20 pressure of 15,000 psi, followed by a classical adsorption/deposition of an aqueous slurry of silver particles onto an α -alumina support. The number of passes of the medium for each consecutive experiment was fixed, and the feed flow rates and processing time were adjusted accordingly. The total number of passes for this series of experiments was held constant at 17.6. Experiments were conducted at varying throat cavitation number, by 25 varying the size of the first orifice. The results are shown in Table 8 below.

Table 8: Variation in silver particle grain sizes

Orifice Sets in./in.	Throat Cavitation Number (calculated)	Silver Grain size (nm)
0.005/0.014	3.07	16.00
0.007/0.014	4.36	21.00
0.009/0.014	5.46	19.20
0.011/0.014	7.93	17.30

Example 16

5

The degree of calcination was examined when using the present invention. Four separate samples of solid ammonium molybdate were calcined for four hours in air to 100°C, 175°C, 250°C and 325°C respectively. XRD data was then taken for each sample. A sample of ammonium molybdate was dissolved in water and fed into an 10 isopropyl alcohol solution (the precipitation agent) just before it passed into a CaviPro™ processor using a 0.012/0.014 inch orifice set. This sample was then filtered and dried at 100°C. XRD data was then obtained for this sample. A comparison of the XRD patterns showed that the sample generated from the present invention had a degree of calcination greater than the sample calcined at 100°C, and about equal to that of the 175°C sample. 15 Considering the residence time of milliseconds for the present invention as compared to 4 hours for the conventional method, the use of the present invention resulted in some in situ thermal calcination.

Example 17

20 In order to evaluate the effect of silver concentration on crystallite size, a series of silver on alumina catalysts were synthesized, with varying concentrations; 1%, 2%, 5%, 10%, and 15 wt% Ag on Al₂O₃. In this synthesis a 20.44 g. aluminum isopropoxide in 100 mL cyclohexane solution was added to 600 mL water that was recycled in the 25 CaviMax (0.075" orifice). After 5 minutes processing, hydrazine was added in a silver to hydrazine ratio of 1. After five minutes processing, a 400 ml silver acetate solution was

fed to the CaviMax (40 mL/min.). After silver acetate addition, the product was processed for 10 minutes (total synthesis time was 30 minutes). The product was pressure filtered, washed with 150 ml isopropanol (to remove the cyclohexane), and washed twice with 150 mL di-H₂O. The samples were dried overnight at 105°C. The 5 Ag/Al₂O₃ samples were calcined for six hours at 400°C. After calcination, the samples were analyzed using XRD. These results are shown in Fig. 3. The XRD of the 400°C calcined material show virtually no reflection for metallic silver indicating that the particles are exceptionally well dispersed. The broad envelope that arises near 35 degrees 10 2 theta could be due to the formation of silver oxide. It is known that silver oxide decomposes at 300°C; thus, if all of the silver has been converted to silver oxide, it consists of very small grain sizes and must be strongly interacting with the aluminum 15 oxide support. The literature reports that a high temperature form of silver oxide may be synthesized, but the literature report indicates that this oxide is normally able to be formed only at temperatures above 1600 K. The unusual behavior of these materials is that the silver component must be formed in very small grains and has provided a catalyst 20 structure which is much different from that of literature reported forms of silver on alumina. It is expected that this catalyst would be very effective in the environmental catalysis area and useful for the reduction of nitric oxide by hydrocarbons. The fact that a high temperature, stable form of silver oxide is obtained in these catalysts may be especially useful for the nitric oxide reduction reaction.

Example 18

Synthesis of Novel Structures for copper modified zinc oxide useful as a catalyst for the synthesis of methanol. A series of experiments were performed precipitating

5 Cu_{0.225}Zn_{0.675}Al_{0.1}, to study its influence of cavitation. Therefore, an aqueous solution was prepared solving 37.514 g (0.1 mol) Al(NO₃)₃*9 H₂O, 60.40 g (0.225 mol) Cu(NO₃)₃*3 H₂O and 124.353 g (0.675 mol) Zn(NO₃)₃*X H₂O in 1000 ml deionized water. As precipitation agents were used an aqueous 0.553 molar (NH₄)₂CO₃ and 1.0 molar Na₂CO₃ solution. The amount on carbonates used was determined experimentally
10 to obtain a pH value of 8. Two different series were performed in the CaviPro. The first series was done using (NH₄)₂CO₃ at a constant pressure of 10,000 psi with the orifices 6-14, 7-14, 8-14, 10-14 and 12-14 (Denoted as Low Pressure Experiments). The second series was done using Na₂CO₃ at a constant pressure of 20,000 psi with the orifices 6-7, 6-10, 6-12 and 6-14 (Denoted as High Pressure Experiments). All samples were washed
15 with water, filtered, dried at 100 °C over night and then calcined at 350 °C for four hours. XRD was taken and the standard investigations were performed. All X-ray patterns were identified as a mixture of ZnO and CuO. Additionally, residual Na₂CO₃ was detected for the second series, which was not removed totally with the washing procedure. Figure 4 reveals a typical diffractogram obtained. Another important feature of the experimental
20 results is shown in Figure 5. The data in this figure indicated that the cavitation processing experiments resulted in different grain sizes of the active component, CuO, and that the strain in these small grain increased as the grain sizes decreased. Furthermore, the classically prepared materials all showed a very low degree of strain.

The analysis of the lattice constants for both oxides shows some very unusual
25 results for methanol synthesis catalysts as judged from prior literature synthesis of this type of catalyst. Fig. 6 shows that the lattice spacing for the c-axis direction in CuO has been shifted to an unusually high value as compared to conventional catalysts for the high pressure experiments. The c axis of the copper oxide is shifted in the high pressure experiment to the same value as that of the zinc oxide. This distortion of the unit cell, is
30 very unusual, and causes the much larger strain detected for CuO in this system. Furthermore, this fact is an indication for epitaxial growth of CuO on ZnO and a novel

structure for this type of catalyst. This is potentially important for the activity of this material in methanol synthesis catalysts. Epitaxy is the growth of a solid compound (here CuO), which tries to imitate the structure of the substrate (ZnO). Due to the different preferred geometric arrangements of Cu^{2+} (quadratic planar) and Zn^{2+} (tetrahedral), it is
5 not possible for one or the other species to grow in that way. The transition from ZnO to CuO can be considered as an interlayer, which has in the lower plane Zn atoms. The next plane would be a layer of O atoms, followed by the first layer of Cu atoms. In that case a kind of 2-dimensional super lattice can be found. Since this appears to be a novel
10 structure for a Cu-Zn-Al-O methanol synthesis catalyst which may be obtained by cavitation processing and at high pressure cavitation processing, it could be important in the eventual catalytic evaluations. Furthermore, the data in Figure 5 show that the copper oxide component can be synthesized in systematically varying grain sizes.

Example 19

15 A series of 2% palladium on alumina/zirconia (10%/90%) support were synthesise in order to produce a catalyst with high surface area, and small metal crystallite size that is stable up to high temperatures (1200 °C). It has been suggested that the alumina acts as a barrier that prevents phase transformation of the zirconia support,
20 and thereby regaining small grain crystallite support and prevention of sintering of the palladium. Four samples were synthesized in the CaviMax (0.073", 0.081"; 0.095", and 0.115"), as well as a classical precipitation. 100 mL of a palladium nitrate solution and 100 mL of a hydrazine hydrate solution was added to a 700 mL water recycle in the CaviMax. This mixture was processed for 30 minutes, after which a zirconium n-
25 butoxide/aluminum isopropoxide in n-hexane solution was added to the synthesis solution. This new solution was processed for an additional 20 minutes after which the samples were pressure filtered and washed. The 1095 °C air calcined material using the 0.115" orifice in the CaviMax is shown in Figure 7. The important aspect of this result is that a palladium supported catalyst was synthesized where high temperature calcination
30 did not cause the catalyst to density to a large grain material which would be expected to have a very low surface area. This type of high temperature stable catalyst would be

expected to have commercial application in turbine combustion used by power companies to generate electricity.

While various embodiments of the present invention have been disclosed, it should be understood that modifications and adaptations thereof will occur to persons skilled in the art. The compositions of the present invention as well as the methods of forming those compositions can be extended to a number of uses and applications. Other features and aspects of this invention will be appreciated by those skilled in the art upon reading and comprehending this disclosure. Such features, aspects, and expected variations and modifications of the reported results and are clearly within the scope of the invention and the invention is limited solely by the scope of the following claims.